Preamble

Multifunctional oxides are being extensively studied owing to their potential use in the development of capacitors, sensors, memory devices, *etc.* This thesis deals with the detailed investigations into the systems possessing promising attributes for use in diverse applications owing to their unique electrical and magnetic properties. High dielectric constant materials, which are non-ferroelectric, have attracted a lot of attention in the past decade. The high dielectric constant behavior of Sr_2TiMnO_6, a double perovskite was revealed for the first time and the extrinsic mechanisms that result in such a behavior has been investigated. The magnetic characteristics of Sr_2TiMnO_6 was very interesting from the perspective of establishing novel ferroic materials. Mn doped $SrTiO_3$ (STO) was investigated for its dielectric and magnetic properties from a similar perspective. Alongside, the dielectric relaxor characteristics of these systems require in-depth physical understanding given their complex relaxation mechanisms. Keeping in mind, the need for functional oxides which exhibit ferroic properties above room temperature (RT) for certain high temperature applications, various compositions belonging to the solid solution $Bi_4Ti_3O_{12}$-m$BiFeO_3$ (m=3,5) were investigated for its ferroelectric and magnetic characteristics.

Chapter 1 gives a brief introduction to the crystal structure of various systems that have been studied. The high dielectric constant behavior arising due to different mechanisms such as intrinsic/extrinsic has been discussed. The basic concepts of ferroic behavior including the dielectric, impedance and magnetic characteristics have been introduced for the benefit of the readers. A detailed literature survey of the work done on various materials from the perspective of the above mentioned concepts have been presented and the motivation for carrying out the work described in the thesis, has been adequately discussed.

Chapter 2 deals with the details of the synthesis methods and characterization techniques that were employed to study various systems.

Chapter 3 concerns the study of structure and magnetic characterization of Sr_2TiMnO_6 (STMO). STMO powders were synthesized by solid-state reaction route and dense ceramics were obtained by subsequently heat treating the compacted powders. Monophasic nature of STMO was confirmed by employing XRD and high resolution XRD data obtained at room temperature was subjected to Rietveld refinement procedure in order to extract the structural information such as lattice parameters, atomic positions, bond-lengths etc. STMO belongs to cubic structure associated with Fm-3m space group. The B-site cation disorderness has been quite high in STMO owing to almost equivalent ionic radii/oxidation states of Mn and Ti occupying the B-site. However TEM studies showed that there were short range ordered regions in an overall disordered lattice. Micro-Raman spectroscopic studies exhibited a first order spectra indicating a lower crystal structure symmetry. IR reflectivity studies supported the observations made from Raman data in addition to ruling out any structural phase transition down to 10 K. The presence of multiple spin states of Mn and the overall electronic structure configuration of STMO was studied with XPS. Magnetization (M) versus temperature behavior of STMO was obtained in the (10 - 300 K) temperature range under an applied magnetic field (H) of 100 Oe. Two peaks at T_1=14 K and T_2=44K respectively were observed in the temperature dependent magnetization studies. The Curie-Weiss fit of the high temperature magnetization data (T > 100 K) yielded an effective magnetic moment value of 4.21 μ_B and 4.52 μ_B for STMO ceramics sintered at 1573 and 1623 K respectively. Unsaturated hysteresis loops (M versus H) were observed for STMO at 10 and 40 K whereas linear M-H behavior was encountered at temperatures $\geq$ 100 K. Possibility of spin glass behavior was ruled out based on AC susceptibility measurements.

In **Chapter 4**, the detailed investigations that were carried out into the conductivity and dielectric properties of STMO in a wide frequency and temperature range were illustrated. DC conductivity (σ_{DC} was measured in a four probe configuration from RT down to 10 K. The conductivity behavior of STMO was anlayzed in two different temperature ranges *i.e.* from 180 - 300 K and 55 K to 180 K. The Arrehnius fit of the σ_{DC} with 1/T behavior was carried out and the activation energy of the charge carriers participating in the conduction process

was obtained. The low temperature data of σ_{DC} with 1/T ($<$ 180 K) was studied under the paradigm of Mott's variable range hopping mechanism of polaronic conduction. Due to the semiconducting nature of STMO, temperature dependent dielectric measurements were constrained to the low temperature range. The temperature dependent dielectric constant (ε_r') recorded in 180-300 K temperature range and 100 Hz-10 MHz frequency range, exhibited a thermally activated relaxation behavior with step-like increase in the dielectric constant with increase in temperature. STMO exhibited high ε_r' values in the order of $\sim 10^5$ (at 300 K) and ~ 240 (at 180 K) and this behavior was akin to CCTO, a giant dielectric constant material reported in the literature. The frequency dependent dielectric constant data of STMO was modeled under the Cole-Cole formalism and the relaxation times involved in the dielectric relaxation were extracted for various temperatures. Analyses of AC conductivity plots for various temperatures indicated the presence of two relaxations.

Equivalent circuit analysis of the complex Z* plots (180 and 300 K) gave the Capacitance (C) and Resistivity (R) values associated with each of the relaxations observed in the impendance behavior. Based on the (R,C) values, the low temperature relaxation (at 180 K) was completely attributed to the grain boundary relaxation (C$\sim 10^{-9}F$) and with increasing temperature, the space charge relaxation (C$\sim 10^{-7}F$) started to appear in the overall behavior. Therefore Maxwell-Wagner relaxation orignating from the microstructural heterogeneity such as grain/grain boundary interface effects, could be the possible reason for the high dielectric constant values exhibited by STMO. Attempts were made to rationalize the extrinsic contribution to the dielectric constant behavior of STMO by carrying out studies with different electrode materials and samples of different thickness. Impedance bahavior of STMO was also studied with different DC bias field ranging from 1 V/cm to 11 V/cm. The space charge relaxation was sensitive to the applied DC bias whereas the response pertaining to the grain boundary relaxation remained unchanged. The Schottky barrier voltage of STMO was calculated by considering the situation similar to that of metal/semiconductor interface. The temperature dependent dielectric behavior (ε_r' and D) of STMO was once again revisited, down to 10 K in order to investigate any possible structural phase transition. The frequency dependent ε_r' was fit with Cole-Cole formalism

which has been corrected for the contribution arising from conductivity. The relaxation time (τ) versus 1/T behavior was fit with Arrhenius equation to extract the activation energy value. Any attempt to implement Voger-Fulcher formalism (used to explain relaxor characteristic) has failed for STMO owing to its high conductivity values that nullifies observation of cooperative phenomena among the dipoles.

Chapter 5 consists of synthesis dependent characteristics of $Sr_{1-x}Mn_xTiO_3$ (x=0.03, 0.05, 0.07 and 0.09). The previous chapter dealt with Sr_2TiMnO_6, a solid solution between $SrTiO_3$ and $SrMnO_3$, where the focus was on the influence of B-site occupation of Mn on the overall dielectric and magnetic behavior. Though we unravelled the colossal dielectric behavior of Sr_2TiMnO_6 pertaining to extrinsic mechanisms such as Maxwell-Wagner polarization, its leaky behavior has been a cause of concern. In an attempt to develop systems with possible ferroic characteristics and at the same time possessing low dissipation factor, $SrTiO_3$ (STO) systems doped with various levels of Mn in the A-site were studied. The primary concern has been to obtain monophasic samples belonging to the above mentioned compositions as the previous reports on this system showed maximum solid solubility upto x=0.03. Three different synthesis methods such as solid-state reaction route, co-precipitation of oxalates and the freeze drying, were employed successively depending on the extent to which phase pure samples belonging to the above compositions could be obtained. High resolution XRD studies revealed the presence of secondary phases such as MnO and Mn_3O_4 for ceramics fabricated from calcined powders obtained by solid-state reaction route. Further, chemical co-precipitation technique was adopted to synthesize powders belonging to compositions x=0.03, 0.05, 0.07 and 0.09. The thermal decomposition behavior of the precipitate was studied to assess the phase formation temperatures. Monophasic samples of x=0.03 and 0.5 were achieved as confirmed by XRD whereas the compositions higher than that indicated the presence of secondary phases. Freeze drying technique was employed in the synthesis of compositions corresponding to x=0.05, 0.07 and 0.09 of Mn doping. The crystallite size of the calcined powders obtained from freeze-drying method was in the range of 35-65 nm. Through optimization of temperatures used for sintering the ceramics, the quantity of secondary phases could be reduced/nullified (as confirmed by XRD)

in the compositions upto x=0.07. However the formation of impurity phases such as MnO and Mn_3O_4 in $Sr_{1-x}Mn_xTiO_3$ has been tricky when high temperatures are adopted to fabricate the samples.

Microstructural studies that were carried out on the ceramics obtained by the different routes revealed a much fine grained nature of those obtained by freeze drying method. Room temperature Micro-Raman studies were carried out to complement the results obtained from XRD regarding the phase purity. The decomposition of multiphonon scattering modes with increasing Mn might indicate possible local structrual distortion due to off-centered position of Mn. Dielectric behavior of samples belonging to the above mentioned compositions were studied at various temperatures (80-300 K) and in the 100 Hz - 1 MHz frequency range. Dielectric constant (ε_r') reduced by almost half for fine grained ceramics derived from powders synthesized by freeze drying method compared to those of solid-state reaction and co-precipitation methods. This behavior is attributed to the dead layer effect that was observed previously in pure and fine grained $SrTiO_3$ leading to a decrease in dielectric constant. In addition, the presence of secondary phases also contributed in general to the decrease in the dielectric constant values.

In **Chapter 6** the detailed studies on the structural, dielectric and magnetic properties of $Sr_{1-x}Mn_xTiO_3$ (x=0.03, 0.05 and 0.07) are reported. Rietveld refinement of XRD data was carried out for the above mentioned compositions that includes monophasic as well as the ones with Mn_3O_4 as secondary phase. The lattice parameter was found to increase with increase in level of Mn doping. XRD studies on Mn doped STO (x=0.5) down to 10 K indicated a structural phase transition from $Pm\bar{3}m$ to $I4/mcm$ around 100 K similar to the case of pure STO. Dielectric measurements were carried out in the 10-300 K temperature range and 100 Hz - 1 MHz frequency range. Relaxor like behavior with broad peaks shifting with increasing frequency within the temperature range of 20 to 65 K was observed. The temperature at the peak maximum (T_m) was found to decrease with increase in Mn doping. The diffuseness parameter and the strength of dispersion were also studied for the above mentioned compositions. The nature of dielectric relaxation for these systems was studied in three different temperature ranges

given by (a) T< 20 K within Barret formalism that models the quantum paraelectric behavior (b) > 100 K analyzed with Curie-Weiss model (c) intermediate temperature range 20K<x<65K studied under semi-empirical Vogel-Fulcher formalism and critical dynamical scaling theory near phase transition temperature (T_c). The unphysical relaxation parameters obtained by invoking Vogel-Fulcher equation was in contrast to those reported previously for similar systems. The dielectric behavior of Mn doped STO involves a complex coexistance of quatum paraelectric behavior and the relaxor characteristics due to the reorientation of polar clusters. By assuming a weak coupling between the two, the experimental temperature dependent dielectric data was corrected for underlying quantum paraelectricity by utilizing the Barrett's equation. The relaxation parameters obtained from the corrected experimental dielectric data were found to be more agreeable.

Magnetic behavior was studied for the above mentioned compositions in the 10-300 K temperature range under both zero field-cooled (ZFC) and field-cooled (FC) conditions. The sample possessing x=0.03 of Mn doping exhibited an overall paramagnetic trend in the temperature dependent magnetization data. Magnetization (M) versus applied magnetic field (H) data too was linear upholding its paramagnetic nature. However, invoking Curie-Weiss law in the high temperature region (> 100 K) yielded a negative Néel's temperature (θ_N) value implying a weak antiferromagnetic interaction present in this system. Temperature dependent ZFC and FC magnetization curvers bifurcated just below the room temperature and saturated hysteresis loops (M versus H) recorded at room temperature proved the existence of strong ferromagnetic interactions in samples with x=0.5 of Mn doping. In order to establish the significant role of impurities in affecting the magnetic properties, magnetic characterization of sample with x=0.05 of Mn doping already consisting of Mn_3O_4 as a secondary phase, was also carried out in detail.

Chapter 7 illustrates the ferroic characteristics of Aurivillius $Bi_4Ti_3O_{12}$-m$BiFeO_3$ (m=3,5) together with the effect of La substitution in m=3 compound given by $Bi_4Ti_3O_{12}$-3$Bi_{1-x}La_xFeO_3$ (x=0.01, 0.05, 0.1 and 0.2). The compounds belonging to the above mentioned compositions were synthesized by employing

the conventional solid-state reaction route. Profile refinement of the X-ray diffraction data was carried out for $Bi_4Ti_3O_{12}$-5$BiFeO_3$ (BFTO5) and the peaks were indexed according to *Fmm2* space group with lattice parameters a=5.46 Å, b=5.49 Å and c= 57.55 Å. For $Bi_4Ti_3O_{12}$-3$BiFeO_3$ (BFTO3) and the La substituted BFTO3 (LBFTO3), the XRD reflections were indexed by profile refinement according to the space group $P2_1am$. The lattice parameters for BFTO3 and the LBFTO3 have been reported. High temperature X-ray diffraction studies in 300 - 1023 K temperature range indicate a structural phase transition from orthorhombic to tetragonal structure around 950 K and the structural phase transition temperature was found to decrease with increase in La substitution of BFTO3. TEM studies on bulk BFTO5 revealed its intergrowth nature and a larger presence of stacking faults/disorderness.

Dielectric measurements (ε'_r) were carried out for all the above mentioned compositions at various temperatures (300-1023 K) in the 100 Hz to 10 MHz frequency range. The peak at 962 K in temperature dependent ε'_r data for BFTO5 accompanied by a peak in the temperature dependent loss (D) behavior was found to be associated with the ferroelectric orthorhombic to paraelectric tetragonal phase transition. Similarly dielectric measurements carried out on BFTO3 exhibited two anomalies at 803 K and 983 K similar to that observed in BFTO5. The peak around 983 K in ε'_r versus temperature curve accompanied by the peak in loss (D) versus temperature curve around the same temperature signifies the ferroelectric orthorhombic to paraelectric tetragonal phase tansition. There was no signature of sharp ferroelectric to paraelectric phase transition for both x=0.01 and x=0.05 La substituted BFTO3 upto 1023 K. However the corresponding peaks in the loss curves were clearly found to shift with increase in frequency suggesting a relaxor behavior. Substitution of La at low levels at Bi-site has been known to induce relaxor characteristics in some of the Aurivillius oxides. For compositions corresponding to x=0.1 and 0.2, conventional ferroelectric to paraelectric like phase transitions were observed at 760 K and 749 K respectively. The transition tempreature (T_c) decreased with increase in the level of La substitution. The DC condution behavior of BFTO5 was investigated in the (300 - 1023 K) temperature range where two different conduction processes owing to electron hopping and oxygen vacancies were identified. Ferroelectric hysteresis loop (P versus E) of

BFTO5 was recorded at room temperature associated with remnant polarization value $2P_r \sim 5.62\ \mu C/cm^2$ and coercive field of 42 kV/cm. Similarly, ferroelectric hysteresis loop with a remnant polarization value $2P_r \sim 8.9\ \mu C/cm^2$ and coercive field of 40 kV/cm was obtained for BFTO3 around 423 K. Detailed magnetization studies were carried out on BFTO5, BFTO3 and the LBFTO3 samples in the 10 - 600 K temperature range. A peak observed around room temperature in the temperature dependent magnetization data for BFTO5 indicates the presence of ferromagnetic interaction which was further corroborated by the observation of magnetization hysteresis loop with finite remnant magnetization (M_r) value.

Chapter 8 deals with the summary and conclusions derived from the work reported in the thesis though each chapter is provided with conclusions and complete list of references. The scope for future work will be discussed at the end of this chapter.